

CHAPTER 5

Thermal Conductivity of Polymers

DONALD E. KLINE

DEPARTMENT OF MATERIALS SCIENCE
PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

DAVID HANSEN ←

MATERIALS RESEARCH CENTER
RENSSELAER POLYTECHNIC INSTITUTE
TROY, NEW YORK

5-1 Mathematical Analysis of Heat Conduction	248
A. Fourier's Law and Thermal Conductivity	248
B. Thermal Diffusivity	249
5-2 Physics of Heat Conduction in Liquids and Solids	250
A. Conduction in Dielectric Crystals	250
B. Conduction in Liquids and Amorphous Solids	252
5-3 Heat Conduction in Polymers	253
A. Amorphous Polymers	253
B. Crystalline Polymers	262
5-4 Polymer Conductivity Data	264
A. Polymethyl Methacrylate (PMMA)	264
B. Polystyrene (PS)	265
C. Polyurethane	266
D. Polyvinyl Chloride (PVC)	266
E. Polyethylene (PE)	270
F. Polypropylene (PP)	272
G. Polyamides	274
H. Polyoxymethylene	274
I. Polyethylene Terephthalate (PETP)	275
J. Polytetrafluoroethylene (PTFE)	276
K. Polychlorotrifluoroethylene (PCTFE)	277
L. Thermosetting Polymers; Epoxies	278
M. Rubbers	279

247

N71 70035

FACILITY FORM 602

(ACCESSION NUMBER)

46

(PAGES)

CR-111632

(NASA CR OR TMX OR AD NUMBER)

(THRU)

None

(CODE)

(CATEGORY)



add: NGL-33-018-003 (Rensselaer)
(Penn State)

N. Other Polymers	281
O. Irradiated Polymers	281
5-5 Conductivity Measurements	282
A. Steady-State Techniques	284
B. Transient Techniques	288
Symbols	289
References	290

5-1 MATHEMATICAL ANALYSIS OF HEAT CONDUCTION

A. Fourier's Law and Thermal Conductivity

Phenomenological analyses of heat conduction problems are based on the validity of Fourier's law which may be stated for isotropic systems by the equation (symbols are defined at the end of the text):

$$q_x = -k \frac{\partial T}{\partial x} \quad (5-1)$$

This law states that the heat flux is proportional to temperature gradient and defines the thermal conductivity as a material property.

Since polymers are often used in an oriented or anisotropic state, it is pertinent to state the more general form of Fourier's law:

$$q_x = -k_{xx} \frac{\partial T}{\partial x} - k_{xy} \frac{\partial T}{\partial y} - k_{xz} \frac{\partial T}{\partial z} \quad (5-2)$$

$$q_y = -k_{yx} \frac{\partial T}{\partial x} - k_{yy} \frac{\partial T}{\partial y} - k_{yz} \frac{\partial T}{\partial z} \quad (5-3)$$

$$q_z = -k_{zx} \frac{\partial T}{\partial x} - k_{zy} \frac{\partial T}{\partial y} - k_{zz} \frac{\partial T}{\partial z} \quad (5-4)$$

These equations recognize that in an anisotropic material the heat flux in a given direction depends not only on the gradient of temperature in that direction but also on temperature gradients in other directions. The thermal conductivity for an anisotropic material is a tensor property which is specified by the nine components, k_{ij} . Since the Onsager reciprocal relations are generally assumed to apply to the thermal conductivity, the number of distinct components of the conductivity tensor is reduced from nine to six by the relationships:

$$k_{xy} = k_{yx} \quad (5-5)$$

$$k_{xz} = k_{zx} \quad (5-6)$$

$$k_{yz} = k_{zy} \quad (5-7)$$

It can also be shown that when the coordinate directions correspond to the directions of principal conductivity, the cross components of the conductivity tensor are zero, and:

$$q_{x^*} = -k_{x^*} \frac{\partial T}{\partial x^*} \quad (5-8)$$

$$q_{y^*} = -k_{y^*} \frac{\partial T}{\partial y^*} \quad (5-9)$$

$$q_{z^*} = -k_{z^*} \frac{\partial T}{\partial z^*} \quad (5-10)$$

If the three principal conductivities of a material are determined, then all the conductivity coefficients for arbitrary coordinate orientation with respect to the principal conductivities may be calculated. If the principal conductivity directions are known, then the conductivities can be measured by standard methods utilizing one-dimensional heat flow. In single crystals it is generally assumed that the principal conductivity directions coincide with the optic axes of the crystal. For polymers the reported characterizations of anisotropic heat conduction have been concerned with uniaxially oriented (stretched) polymers where it is tacitly assumed that the orientation (stretched) direction is a principal conductivity direction and that the other principal directions are equivalent and may be chosen anywhere perpendicular to the orientation direction. The uniaxially oriented polymer is characterized by two conductivities, k_{\parallel} , parallel to the orientation, and k_{\perp} , perpendicular to the orientation. Presumably, a biaxially oriented polymer will have three principal conductivities, but no studies of heat conduction in biaxially oriented polymers have been reported.

B. Thermal Diffusivity

The analysis of conduction heat transfer problems typically begins with the insertion of Fourier's conduction law into an energy balance. For simple conduction in an isotropic material with constant properties, this leads to the familiar equation (in Cartesian coordinates):

$$\alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) = \frac{\partial T}{\partial t} \quad (5-11)$$

in which α is the thermal diffusivity. It is related to the conductivity by the equation

$$\alpha = \frac{k}{\rho c_p} \quad (5-12)$$

where ρ is the density and c_p is the heat capacity. Whereas the thermal

conductivity characterizes the capability of the material to conduct heat, the thermal diffusivity characterizes the capability of the material to transmit a temperature or the time scale required to equilibrate with a temperature field.

5-2 PHYSICS OF HEAT CONDUCTION IN LIQUIDS AND SOLIDS

The physics of heat conduction is concerned with the description of the mechanisms, on a molecular scale, by which thermal energy is conducted through a material. Such description can and does lead to insights on the variations in thermal conductivity with temperature, pressure, and structure of a material. In gases, heat is conducted primarily by the diffusive motion of molecules, which can be quantitatively described by the kinetic theory of gases. In metals heat is conducted primarily by the mobile electrons. In dielectric solids and liquids, which include most polymers, heat is conducted by the interactions of the thermal vibrations of molecules and their component atoms.

A. Conduction in Dielectric Crystals

The theory of heat conduction in dielectrics can be approached most simply by considering first a perfectly ordered atomic crystal. Einstein developed expressions for the heat capacity of such crystals by considering each atom as an oscillator in harmonic motion. This treatment of the heat capacity was extended by Debye who considered the coupling of the oscillations or vibrations. He also introduced the idea that the energy of these vibrations, the thermal energy of the crystal, was quantized. This led to the concept of a quantum of lattice vibrational energy now called a phonon. The crystal lattice then becomes a medium which contains the mobile phonons or lattice energy packets. Analyzing heat conduction in terms of the diffusive motion of an ideal phonon gas leads directly to an equation for the thermal conductivity:

$$k = \frac{1}{3} C u \lambda \quad (5-13)$$

where C is the phonon heat capacity (per unit volume), u is the phonon velocity, and λ is the phonon mean free path. Generally u is equated to the velocity of sound (velocity of propagation of vibrations through the lattice) and C to the heat capacity per unit volume ($C = \rho c_p$). Generally in analyzing heat conduction it is pertinent to consider only those contributions to the heat capacity from vibrations active in the conduction of heat.

In a perfect crystal with perfectly harmonic vibrations, there would be no mechanism for phonon scattering and the thermal conductivity would be infinite. However, the anharmonic aspects of the thermal vibrations lead to a conduction resistance characterized by phonon-phonon scattering. The data of Berman et al. (1) reproduced in Fig. 5-1 illustrate the effects of temperature on conduction in dielectric crystals. At temperatures near absolute zero the thermal conductivity is small, reflecting the small heat capacity. As the temperature increases, the conductivity increases in line with the increasing heat capacity. The phonon mean free path, at these low temperatures where the vibrations are very nearly harmonic, is large and is indeed sensitive to the size of the crystals; i.e., the phonon mean free path may be limited by crystal dimensions. As the temperature increases further, the heat capacity increases less rapidly, approaching a nearly constant value, while the lattice vibrations become increasingly anharmonic leading to decreasing phonon mean free path. Consequently the thermal conductivity reaches a maximum with increasing temperature and then declines rapidly. The thermal conductivity of sapphire at 40°K is four orders of magnitude larger than its value at 300°K. Peierls (2) has shown

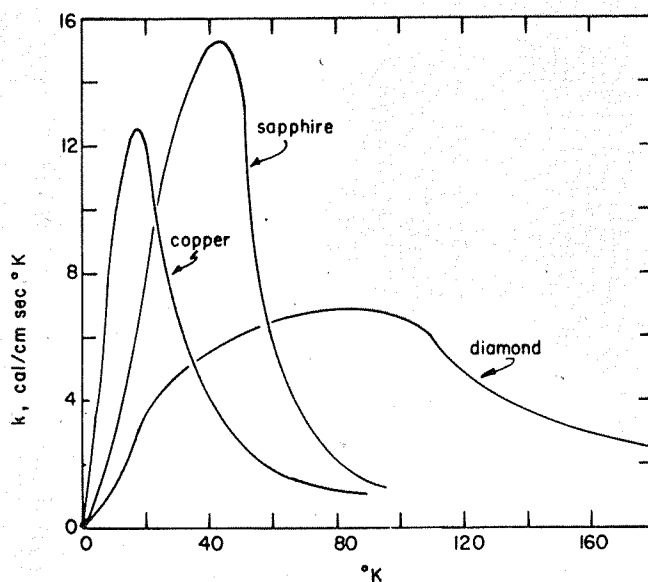


Figure 5-1. Thermal conductivity as a function of temperature for crystalline solids [Berman et al. (1) on copper, sapphire, and diamond].

that phonon-phonon scattering depends primarily on phonon concentration and hence is directly proportional to temperature. At higher temperatures, where the heat capacity is often nearly constant, the thermal conductivity is proportional to the phonon mean free path which varies inversely proportional to temperature. A linear relationship between k and $1/T$ has been verified for many dielectric crystals.

B. Conduction in Liquids and Amorphous Solids

The phonon theory of heat conduction is of limited usefulness in analyzing heat conduction in liquids and amorphous solids, inasmuch as the absence of an ordered lattice leaves the concept of a phonon with doubtful meaning. A striking illustration of the difference in heat conduction between crystalline and amorphous dielectrics is provided by the data of Berman et al.(3). The thermal conductivity of quartz crystal was measured as a function of temperature. The quartz crystal was then irradiated to introduce defects into its structure and the thermal conductivity was measured again. This procedure was re-

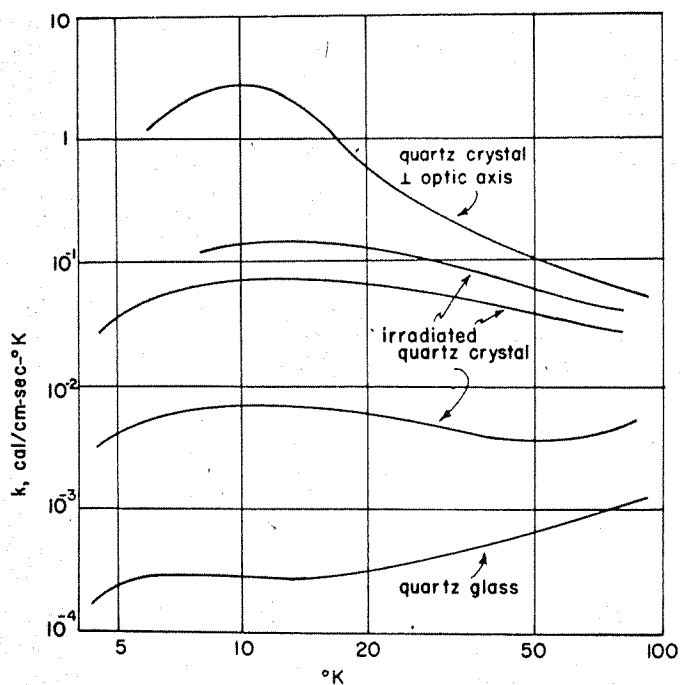


Figure 5-2. Thermal conductivity of quartz crystal, glass, and irradiated crystal [Berman et al.(3)].

peated several times until the quartz crystal had been effectively converted to a glass. Figure 5-2 is a reproduction of the results. The upper curve shows the typical conductivity-vs.-temperature behavior of a crystalline substance, but with increasing doses of radiation the thermal conductivity decreases. The lower curve is for a quartz glass. The conductivity is less than for the ordered crystal, but increases rather than decreases with temperature. Roughly, the temperature dependence of thermal conductivity of a glass can be interpreted as corresponding to a near-constant mean free path whence the thermal conductivity follows the increase in heat capacity with temperature.

In liquids the thermal conductivity is generally less temperature sensitive than in glasses and may decrease with increasing temperature due to thermal expansion. Some materials will show a maximum in the thermal conductivity at the glass transition temperature.

At very low temperatures the wavelengths of phonons become large compared to atomic dimensions, and larger-scale structural features can be factors in heat conductivity. At very low temperatures the simple phonon theory for single crystals or homogeneous amorphous substances predicts conductivity proportional to temperature.

5-3 HEAT CONDUCTION IN POLYMERS

A. Amorphous Polymers

1. TEMPERATURE AND PRESSURE DEPENDENCE

The thermal conductivity of polymethyl methacrylate has been measured from 1°K to 400°K, giving a fairly complete picture of the temperature dependence of thermal conductivity for an amorphous polymer. Reese(4) combined his own measurements at low temperatures with data of Eiermann(5) and Berman(6) to get the results which are summarized in Fig. 5-3. As Reese points out, the general features of these thermal conductivity data are in accord with the theory of heat conduction in glass, proposed by Klemens(7). Over most of the temperature range the phonons are scattered by the disordered, amorphous structure giving a constant mean free path and a thermal conductivity proportional to the volumetric heat capacity. At low temperatures Klemens suggests that the phonon wavelength becomes large compared to the molecular disorder and predicts that mean free path should be proportional to the square of the phonon wavelength, leading to a linear relationship between thermal conductivity and

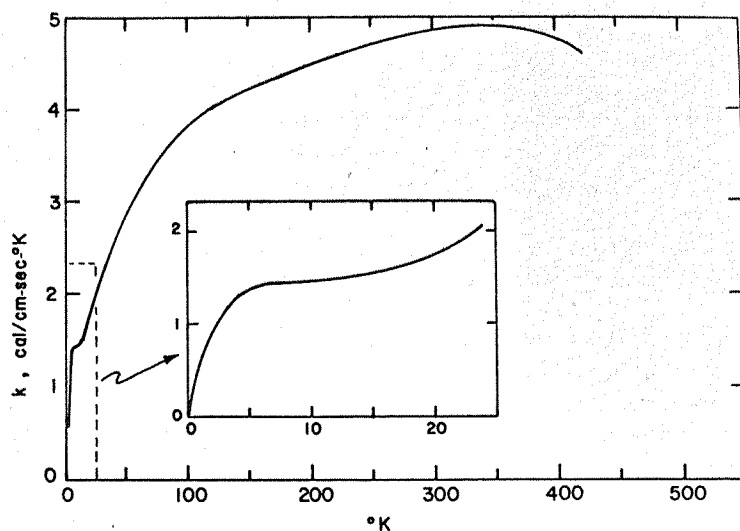


Figure 5-3. Thermal conductivity of polymethyl methacrylate as a function of temperature [Reese (4)].

temperature. Reese's data confirm Klemens' prediction in the region 1°K to 4°K, but the data from 4°K to 25°K diverge from the Klemens theory. Reese was able to eliminate this discrepancy by considering one-dimensional vibrations along the polymer molecule separately from other contributions to the heat capacity, and assigning these vibrations a separate mean free path. In this way Reese fitted a theoretical curve to the experimental data to better than 10% from 1°K to the glass temperature. This agreement is excellent considering the inherent difficulty of obtaining precise thermal conductivity data, and the fact that the data were taken by three different investigators on two different samples. (Reese used Berman's sample for some of his measurements.)

While the phonon theory of heat conduction in amorphous solids, as adapted by Reese for polymers, apparently gives a satisfactory description of the general features of the temperature dependence over a wide temperature range, it does not deal with the effects of transitions, particularly the glass transition. Eiermann and Hellwege(23) have indicated that behavior in the vicinity of the transition may be related to thermal expansion effects. The thermal conductivities of polymer melts remain very nearly constant as a function of temperature. The similarity in thermal conductivity behavior in the vicinity of the glass

transition has been pointed up by Frisch and Rogers(9) who, by using reduced coordinates, were able to represent data for a number of polymers on a single graph. They also attempted correlation of thermal conductivity with other transport properties, but the limited data available were insufficient to establish the validity or usefulness of these correlations.

In comparing the thermal conductivities of polymer melts, as Shoulberg(10) has done from diffusivity data, one notes that all the data fall in the vicinity of 5×10^{-4} cal/cm-sec-°K, with the exception of polyethylene which is somewhat higher. Shoulberg points out that, for the vinyl polymers, thermal conductivities of the melts apparently decrease with increasing size of substituent groups. However, the data are insufficient to permit refinement of this generalization.

The effect of pressure on thermal conductivity has apparently not been studied except for the experiments of Lohe(11) who recorded approximately a 5% increase in the thermal conductivity of molten polyethylene when the pressure was increased from 1 atm to 300 kg/cm².

A specific, curious temperature effect that has some practical significance was noted by Anderson et al.(12) in their experiments below 1°K. Whereas inorganic glasses have conductivity proportional to temperature in this range, the organic polymers (Teflon, Kel-F, Nylon, epoxy) all showed thermal conductivity decreasing more than linearly with decreasing temperatures. While the reasons for this behavior are not clear, the data indicate that the polymers may be superior thermal insulating materials at very low temperatures.

2. MOLECULAR WEIGHT DEPENDENCE

The first significant study of the effect of molecular weight on the thermal conductivity of a polymer was reported by Ueberreiter and Otto-Laupenmühlen(13) who measured conductivities of polystyrene fractions having molecular weights of 860, 2300, and 3650. Their data, both above and below the glass transition temperature, consistently indicate that the higher molecular weight polymer has the higher thermal conductivity. The authors reasoned that the effect was due to the fact that energy could be transmitted more readily along the polymer molecule than between molecules.

Similar reasoning was incorporated into a theoretical analysis of the molecular weight effect by Hansen and Ho(14). This theory predicts that the thermal conductivity should increase as the square root of the weight average molecular weight at low molecular weights, and become

independent of molecular weight at high molecular weights. The data of Hansen, Ho, and Kantayya(14,15) on polystyrene and molten polyethylene apparently agree with the general predictions of the analysis. These data are reproduced in Figs. 5-4 and 5-5. For any polymer it is pertinent to know the molecular weight range over which the thermal conductivity varies significantly. Unfortunately, the theory of Hansen and Ho will not predict this *a priori*. Figure 5-4 indicates that the conductivity of polystyrene is independent of molecular weight above a degree of polymerization of 1000, while the polyethylene curve (Fig. 5-5) does not level off until a degree of polymerization greater than 10,000 is reached.

In Hansen and Ho's analysis the thermal conductivity is indicated to be sensitive to the linear extent of a molecule, suggesting that, for branched and linear homologs of equal molecular weight, the linear polymer should have the higher thermal conductivity. Some support for this view comes from data of Tomlinson, Kline, and Sauer(16) and Hennig, Knappe, and Lohe(17) on melts of linear and branched polyethylene, showing lower conductivity for the branched polymer. When Tomlinson et al. irradiated the branched polyethylene, its melt conductivity increased with increasing radiation dosage to a limiting value of 6.6×10^{-4} cal/cm-sec-°K, essentially the same value determined by Hansen and Ho for molten, high molecular weight, linear polyethylene.

Polymers are frequently used with low molecular weight plasticizers which change thermal as well as mechanical properties. Ueberreiter and Purucker(18) first observed this effect in polystyrene blended with hexachlorodiphenyl. Sheldon and Lane(19) measured conductivities of polyvinyl chloride blended with dialphanylphthalate, and others have reported data generally showing that the addition of plasticizers will decrease thermal conductivity. (See also Section 5-4.) Hansen and Ho(14) have shown that when the thermal conductivity is plotted versus the square root of weight fraction polymer the data of refs.(18,19) yield a straight line. They note that this form of plot is equivalent to a graph versus the square root of molecular weight obtained by averaging polymer and plasticizer molecular weights. The thermal diffusivity data of Ueberreiter and Purucker plotted in this way are shown in Fig. 5-6.

All of the experimental data on the effect of molecular weight reported to date have been limited to a fairly narrow temperature range, and there is little data on polymers other than polystyrene and polyethylene. Lohe(20) recently reported some molecular weight-conductivity data on polymethylsiloxane and polyethyleneglycol. Several authors

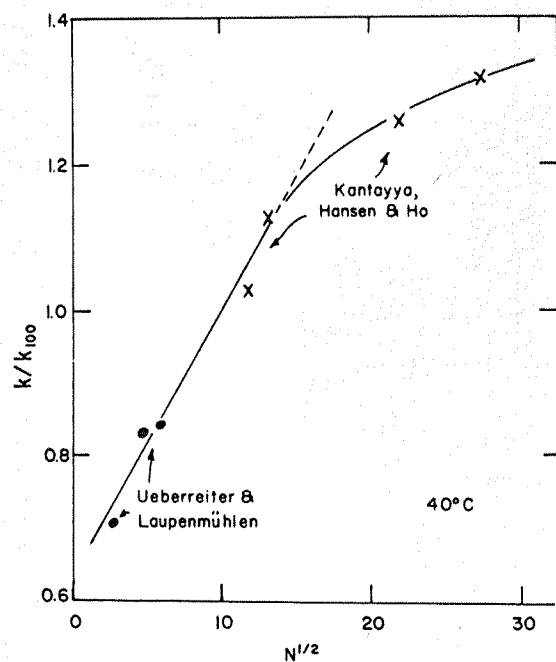


Figure 5-4. Thermal conductivity of polystyrene vs. square root of degree of polymerization. Conductivities normalized to value at degree of polymerization 100 [Hansen et al. (15)].

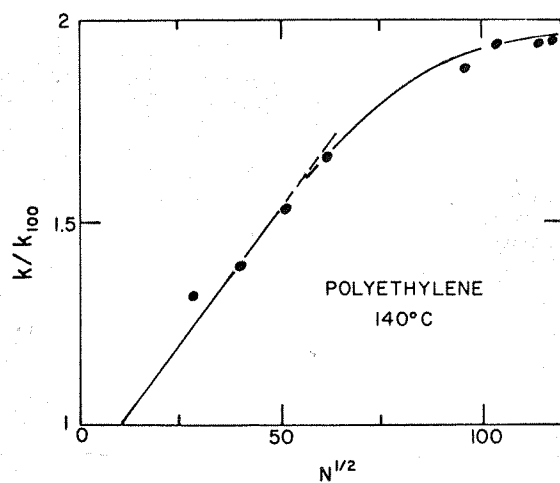


Figure 5-5. Thermal conductivity of molten polyethylene vs. square root of degree of polymerization. Conductivities normalized to value at degree of polymerization 100 [Hansen and Ho (14)].

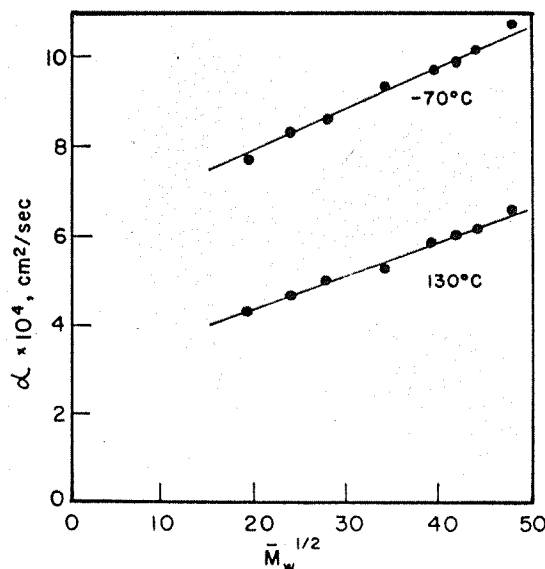


Figure 5-6. Thermal diffusivity of polystyrene blended with hexachlorodiphenyl vs. square root of weight average molecular weight [Ueberreiter and Purucker (18)].

have noted wide discrepancies in reported thermal conductivity values of the same polymer. These discrepancies exceed that which would be expected from experimental error alone and may be due to structural differences such as molecular weight and branching. However, more conductivity data on characterized samples covering broader temperature intervals will be necessary to assess the sources of present discrepancies.

3. MOLECULAR ORIENTATION DEPENDENCE

When a polymer is oriented as by stretching or cold-drawing, the anisotropy of structure is reflected in a corresponding anisotropy in properties. One of the earliest characterizations of thermal conductivity in oriented polymers was reported by Tautz (21) in 1959. Tautz's data, reproduced in part in Fig. 5-7, showed the thermal conductivity of rubber as a function of degree of stretching and vulcanization. The sensitivity of thermal conductivity to orientation apparently increased and then decreased with further vulcanizing. Most striking was the fivefold increase in thermal conductivity observed by Tautz on a highly oriented specimen.

A comprehensive study of an anisotropic conductivity in oriented

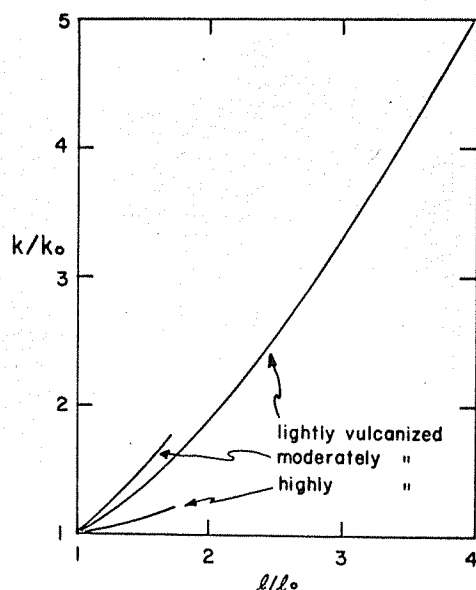


Figure 5-7. Thermal conductivity of rubber (parallel to stretching) as a function of extension ratio [Tautz(21)].

polymers has been reported by Eiermann, Hellwege, Hennig, and Knappe in a series of papers(22-29). These researchers measured conductivities both parallel and perpendicular to the direction of stretching on a variety of oriented amorphous polymers and elastomers. One set of their data is reproduced in Fig. 5-8, a graph of relative thermal conductivity versus relative extension. These data indicate large differences among different polymers in the magnitude of the orientation effect on thermal conductivity, but all show an increase in conductivity parallel to stretching with a decrease normal to the stretch direction. In polyvinylchloride at 100% extension the ratio of k_{\parallel} to k_{\perp} is almost 2 while in polystyrene at 600% extension the ratio is only 1.5. Eiermann and co-workers(22-29) have analyzed the conductivity of oriented polymers in terms of a model comprising low thermal resistances (intramolecular bonds) and high thermal resistances (intermolecular, van der Waals bonds). Stretching the polymer orients the low resistances preferentially parallel to the stretching direction and the high resistance preferentially perpendicular to the stretching direction. From this model of high and low resistances acting in series and parallel, they derived the following equation

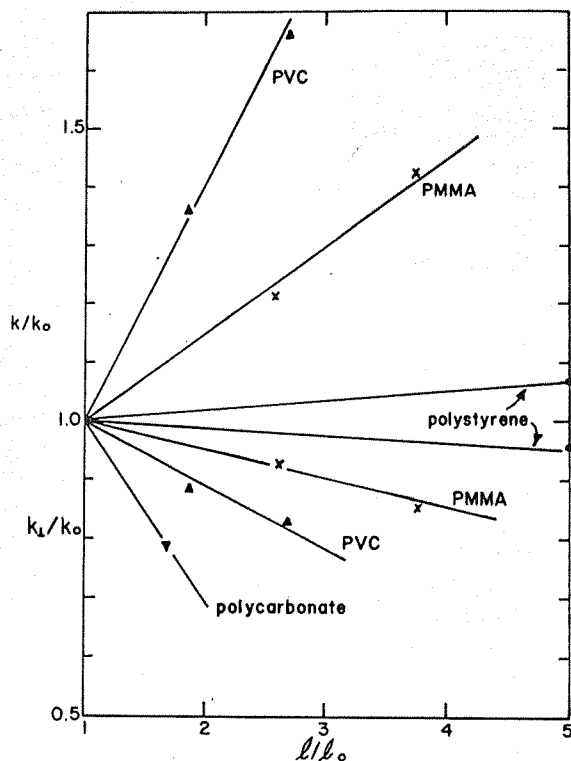


Figure 5-8. Thermal conductivity as a function of extension [Hellwege et al. (24)].

relating the anisotropy in thermal conductivity to the conductivity of the unoriented polymer:

$$\frac{1}{k_{\parallel}} + \frac{2}{k_{\perp}} = \frac{3}{k_0} \quad (5-14)$$

The data on a variety of amorphous polymers were found to agree with this relationship, including data on polymethyl methacrylate from -190°C to 50°C . While Eq. (5-14) very successfully correlates the anisotropy in conductivity of oriented, amorphous polymers, it does not say anything of the difference in magnitude of the anisotropy among different polymers. However, Eiermann and co-workers (22-29) have also successfully applied their model analysis to other properties such as thermal expansion and compressibility. From this they predict relationships between the properties such as the following equations, relating thermal conductivities and the coefficients of linear thermal

expansion:

$$\frac{k_0}{k_{\parallel}} = \left(0.8 \times \frac{\beta_{\parallel}}{\beta_0}\right) + 0.2 \quad (5-15)$$

$$\frac{k_0}{k_{\perp}} = \left(0.8 \times \frac{\beta_{\perp}}{\beta_0}\right) + 0.2 \quad (5-16)$$

Their experimental verification of these relationships is summarized in a graph of their data reproduced in Fig. 5-9.

Hansen and Ho(14) also applied their analysis of the thermal conductivity of polymers to a prediction of the orientation effect, obtaining the relationship,

$$\frac{k_0}{k_{\perp}} = \left(\frac{k_{\parallel}}{k_0}\right)^{1/2} \quad (5-17)$$

They also predicted that, barring a transition, the change in conductivity with stretching should be linear with the molecular orientation. While Eq. (5-17) is very different in form from Eiermann's Eq. (5-14), it does not predict very different numerical results within the bounds where experimental data are available.

Recently, Washo(30) has extended the analysis of Hansen and Ho and predicts a relationship between molecular weight and orientation

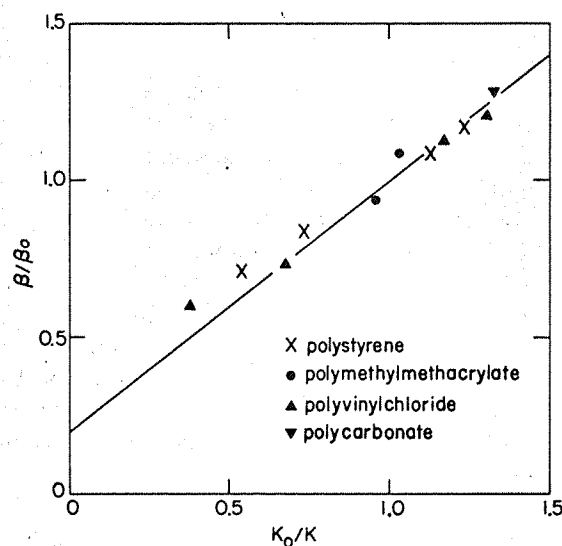


Figure 5-9. Relationship between anisotropy in thermal conductivity and linear thermal expansion [Hellwege et al.(24)].

sensitivity of the thermal conductivity. However, only limited data are given showing a low molecular weight polymethyl methacrylate to be more orientation sensitive than a specimen of higher molecular weight.

As all of the reported data indicate, orientation can induce a significant anisotropy in the thermal conductivity of polymers, which must be considered in analysis of heat transfer in these materials. Presumably, in biaxially oriented materials, three principal conductivities are needed to characterize the material. The derivation of Eqs. (5-14) and (5-17) can be modified to consider biaxial orientation, but no experimental data are available.

Processes such as extrusion generally require heat transfer to a polymer melt, under shear, which may be significantly oriented. While the effects of orientation on conductivity of a melt are expected to be similar to the effects on a solid, amorphous polymer, there have been no reports of experimental characterization of anisotropic conductivity in a polymer melt.

B. Crystalline Polymers

In comparison with the amorphous polymers, crystalline polymers are characterized by a more ordered, denser structure which, in general, yields a higher thermal conductivity. The difference between the amorphous and crystalline polymers with respect to heat conduction may be characterized as a lower resistance to intermolecular transfer in the crystalline polymer. Hence, it might be expected that the conductivity of crystalline polymers would be less sensitive to a parameter such as molecular weight. Indeed, Hansen and Ho(14) observed a significant molecular weight effect in the conductivity of molten polyethylene, but discerned no difference in thermal conductivity among crystalline polyethylenes of different molecular weights. For the same reasons, one would expect less effect of molecular orientation on the conductivity of a crystalline polymer than is observed with amorphous polymers. On the other hand, the crystal structure of polymers is itself highly anisotropic and when oriented could yield significant anisotropy in heat conduction properties. No experimental or theoretical characterization of the thermal conductivity of oriented, crystalline polymers has been reported.

The most extensive studies on heat conduction in crystalline polymers have been reported by Eiermann(31), who measured thermal conductivity of polyethylene, polyoxymethylene, polypropylene, and polyethylene terephthalate from -190°C to $+100^{\circ}\text{C}$. He found the

thermal conductivity-temperature relationship to be sensitive to density. For example, an annealed, linear polyethylene ($\rho = 0.982 \text{ gm/cm}^3$) has a conductivity of $2.8 \times 10^{-3} \text{ cal/cm-sec-}^\circ\text{C}$ at -190°C which decreases to 1.1×10^{-3} at $+100^\circ\text{C}$. A low density, branched polyethylene ($\rho = 0.918$) has a conductivity of only $0.75 \times 10^{-3} \text{ cal/cm-sec-}^\circ\text{C}$ at -190°C , which increases slightly with temperature to a maximum of 0.9×10^{-3} at about -50°C from which it declines to 0.6×10^{-3} at $+100^\circ\text{C}$. However, Eiermann(32) found that some of the wide differences in thermal conductivity of different specimens of the same crystalline polymer could be correlated on the basis of a simple model. Considering the polymers to consist of a composite of amorphous and crystalline material, Eiermann analyzed his data on the basis of a hypothetical conductivity k_c of a perfectly crystalline polymer, and k_a , the thermal conductivity of completely amorphous polymers. The volume fraction or "per cent crystallinity" was assigned in the usual way from density data, and Maxwell's equation was used to calculate k_c and k_a from data on the real polymers(32). When treated in this way, Eiermann's data showed k_a to be proportional to temperature and k_c to the reciprocal of temperature. This is the behavior predicted from phonon theory for amorphous and crystalline dielectrics. Hansen and Ho(14) and Sheldon and Lane(33) have analyzed their data on polyethylene in similar fashion, and confirm Eiermann's findings.

Other studies on heat conduction in crystalline polymers include the observations of Hsu, Kline, Tomlinson, and Sauer(16,34,35), Hattori(36), and Sheldon and Lane(33) on the effects of nuclear radiation. These are discussed in Section 5-4,O. Effects of crystal morphology have not been studied, per se, with respect to heat conduction in polymers. Also lacking is any extensive study of thermal conductivity of crystalline polymers at very low temperatures.

In addition to the general trends in conductivity-temperature graphs for crystalline polymers, one sees local bumps or discontinuities. These may reflect various transitions, and indeed Tomlinson, Kline, and Sauer(16) have related them to dynamic mechanical spectra observations on the same samples. Steere(37) has even suggested the use of thermal conductivity measurements to study polymer transitions, and has demonstrated the potential of the technique with some observations on transitions in polyethylene terephthalate, polytetrafluoroethylene, and polypropylene.

5-4 POLYMER CONDUCTIVITY DATA

In this section a general discussion of thermal conductivity data will be presented. Where sufficient data have been accumulated on a given polymer, it will be discussed separately. It is intended that the discussion be reasonably extensive, realizing that space limitations prevent discussion of every existing reference. The work cited will hopefully provide a core from which the reader can consult the literature in further detail and locate references on a given subject or material. For convenience, thermal conductivity unit conversion factors are given in Table 5-1.

A. Polymethyl Methacrylate (PMMA)

Polymethyl methacrylate has been a primary material for investigation of the process of thermal conduction in amorphous polymers. Studies have included the low temperature behavior, the effect of the glasslike transition, effects of chain orientation, and behavior of the conductivity in the melt. Thermal conductivity data for PMMA have been reported by Reese(4,38), Hattori(39), Eiermann and co-workers (22,23,40), Berman(6), Lohe(11,42), Shoulberg and Shetter(44), Eiermann and Hellwege(23), Holzmüller and Münx(45), Kirichenko, Hennig, and Knappe(46), and Knappe(47). Orientation effects have been investigated by Eiermann(26) (for stretched and unstretched materials), Hellwege et al.(24), and Hansen and Ho(14). Thermal diffusivity data have been presented for temperatures from 25° to 325°C by Shoulberg(10) and, for some temperatures above room temperature, by Chung and Jackson(48).

A combination of Reese's low temperature data with that of others [Eiermann(22) and Berman(6)] were summarized in Fig. 5-3 in a previous section. The conductivity increases from a near-zero value

TABLE 5-1
Thermal Conductivity Unit Conversion Factors

g-cal/cm ² -sec	w/cm ²	w/in. ² -°C/in.	Btu/ft ²	kg-cal/m ² -hr	Btu/ft ² -hr
1.0	4.19	10.63	242.0	360.0	2903.0
0.239	1.0	2.54	57.8	86.0	694.0
0.094	0.394	1.0	22.8	33.9	273.0
4.13 × 10 ⁻³	0.0173	0.0440	1.0	1.488	12.00
2.788 × 10 ⁻³	0.0116	0.0295	0.672	1.0	8.06
0.344 × 10 ⁻³	1.442 × 10 ⁻³	3.66 × 10 ⁻³	0.0833	0.124	1.0

slightly above 0°K to 1×10^{-4} cal/cm-sec-°K at 2.5°K and to 4×10^{-4} cal/cm-sec-°K near 125°K. Values continue to increase with increasing temperature to a maximum near 350°K followed by a slight downward trend. Data of Shoulberg and Shetter(44) have shown that the conductivity typically is independent of temperature up to the glasslike transition temperature, and then decreases with temperature up to 160°C (Fig. 5-10). A discussion of the implications of the PMMA data thus far reported was given in Section 5-3.

B. Polystyrene (PS)

Various aspects of thermal conductivity in polystyrene have been studied. Ueberreiter and co-workers(13,18,49,50) reported data for k , α , c_p , and v concerning the effect of molecular weight, the effect of plasticizing, and the effect of cross-linking via divinyl benzene. Reese and Tucker(51) reported data at low temperatures (below 5°K); Holzmüller and Münx(45) from 20° to about 130°C; Hattori(36,52,53) (k and α) from 20° to 120°C; Kirichenko et al.(46) from 30° to 75°C; Cherkasova(54) from 25° to 95°C; Kline(55) from room temperature to about 100°C; and Lohe(42) from 100° to 250°C (in the melt). Shoulberg(10) has also presented diffusivity data from near the glass temperature to about 300°C.

Hellwege, Hennig, Knappe, and Semjonow(24,47,56) have presented data for c_p and k , including the effect of orientation by stretching. The studies of Hansen, Kantayya, and Ho(15) included molecular weight dependence in polystyrene and molten polystyrene (some PS data are given in Fig. 5-4).

Much of the data reported in the literature has been compiled and

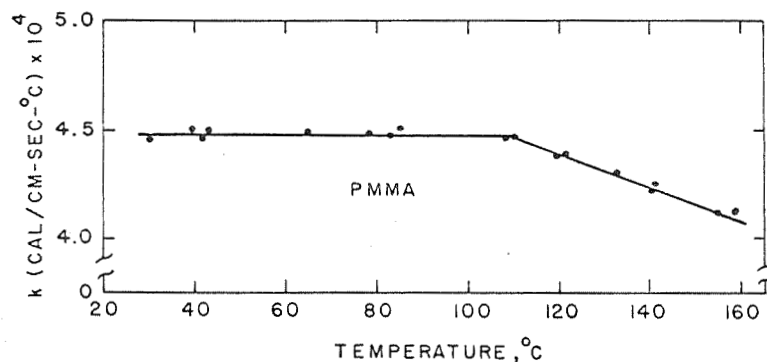


Figure 5-10. Thermal conductivity of polymethyl methacrylate [Shoulberg and Shetter(44)].

evaluated in a study by Carwile and Hoge(57). A summary of their findings is given in Fig. 5-11 where they have also drawn a line representing their selection of probable thermal conductivity values as a function of temperature. For the most part data reported by investigators so far tend to exhibit an increase in conductivity with temperature but an identifiable maximum may also occur. For solid PS the maximum would appear to occur near the glass temperature while this value would appear to be exceeded by a further rise in conductivity with increasing temperature in the melt. It should be noted that all results thus far reported apparently concern atactic PS. No results have been reported for isotactic crystalline PS.

C. Polyurethane

Thermal conductivity data for polyurethanes have been reported by Knappe(47) and Cherkasova(54). These investigators have not described in detail the preparation and analysis of their materials. Their results differ in that Cherkasova's(54) data exhibit an increase from about 3.4×10^{-4} cal/cm-sec-°C at 25°C to about 4.6×10^{-4} cal/cm-sec-°C at 90°C (Fig. 5-12), and results of the Knappe(47) investigation using a partly crystalline material show a decrease from about 7.5×10^{-4} cal/cm-sec-°C at 15°C to 6.2×10^{-4} cal/cm-sec-°C at 100°C. If the material used by Cherkasova was almost completely amorphous rather than appreciably crystalline in nature, as that reported by Knappe, it could conceivably account for the difference in results obtained by the two investigators.

D. Polyvinyl Chloride (PVC)

Polyvinyl chloride is usually considered to be a primarily amorphous polymer. Quantitative estimates of the per cent crystallinity are difficult to obtain. Eiermann, Hellwege, and Knappe(58) reported thermal conductivity data for PVC showing a gradual increase from 3×10^{-4} cal/cm-sec-°K at -180°C to a maximum of slightly greater than 4×10^{-4} cal/cm-sec-°K near 40°C and decreasing only slightly to 90°C. Knappe(47) reported a relatively temperature-independent value of 4×10^{-4} cal/cm-sec-°K from 10°C to 100°C. In this temperature range, Knappe(47) also reported an over-all decrease in conductivity with increasing plasticizing concentration. Holzmüller and Münx(45) presented results from the range 25° to 75°C which showed a small peak followed by a small dip at 45°-55°C superimposed on a nearly-constant thermal conductivity level.

Sheldon and Lane(19) measured thermal conductivity of the PVC

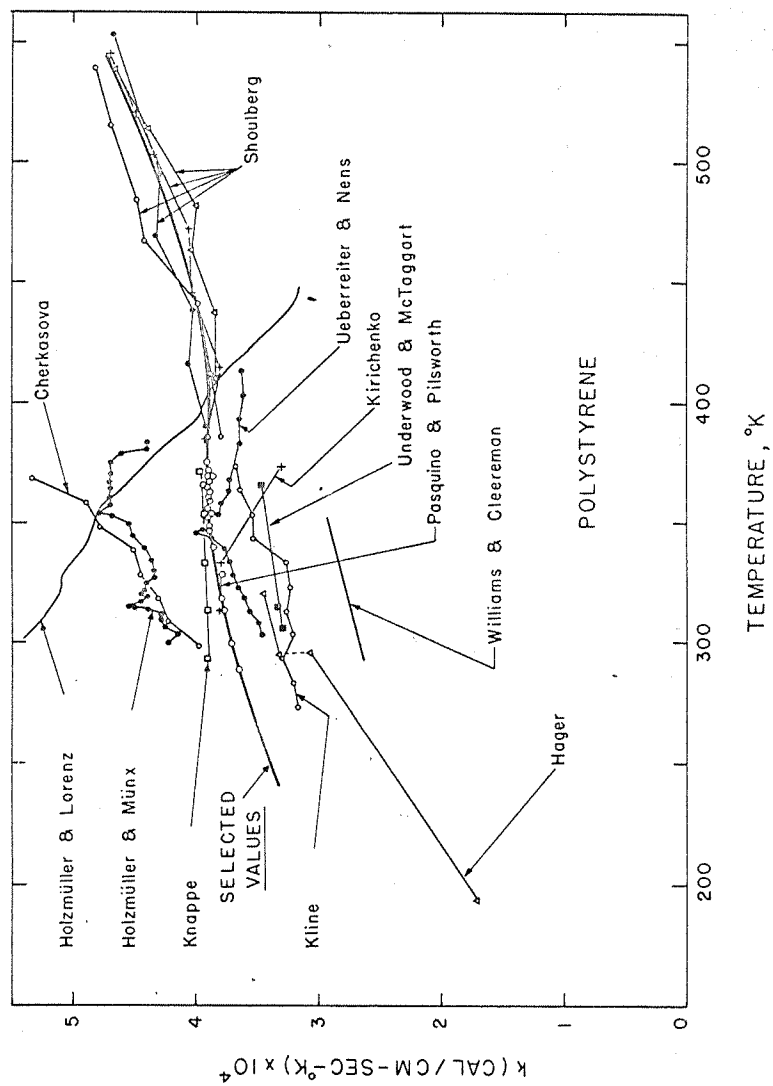


Figure 5-11. Thermal conductivity of polystyrene [Carwile and Hoge(57); for references in this figure see (57)].

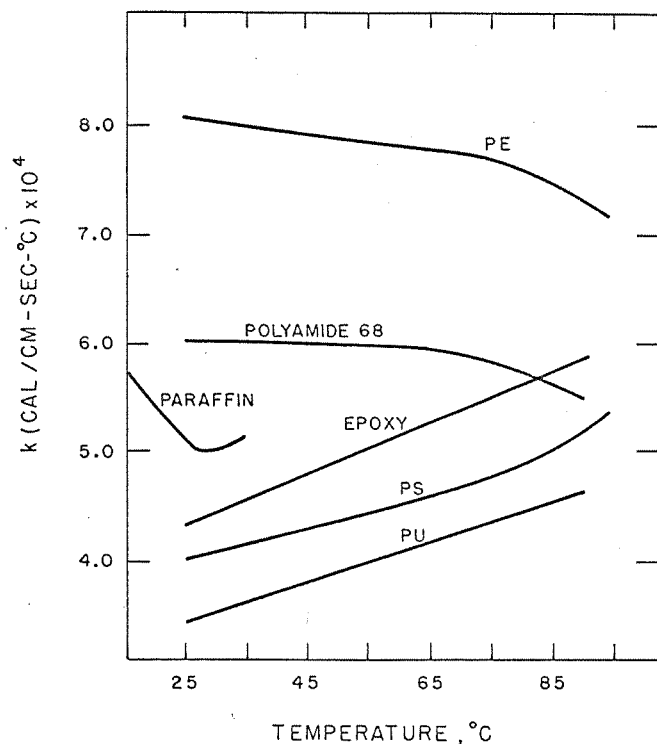


Figure 5-12. Thermal conductivity of PS, PE, PU, paraffin, epoxy, and polyamide 68 [Cherkasova(54)].

specimens with varying plasticizer content (0, 20, 26, 30, 36, 40%) from 15°–98°C and found the conductivity of the unplasticized sample (Fig. 5-13) to increase gradually up to the glass temperature and then to begin to decrease. Maximum values were about 4×10^{-4} cal/cm-sec-°K. With the addition of plasticizer, the glass temperature of PVC decreases and this is apparently reflected in the thermal conductivity; i.e., the maximum in the thermal conductivity shifts to lower temperatures with increasing plasticizer concentration. Near 100°C the conductivity of the 40% plasticized sample was reduced to about 3.4×10^{-4} units. Extrapolations of the thermal conductivity were also made to 0% and 100% plasticizer concentrations for data at 25°C from plasticized specimens and these values (Fig. 5-14) were compared to other measurements and calculations.

Others have also observed changes in thermal conductivity with

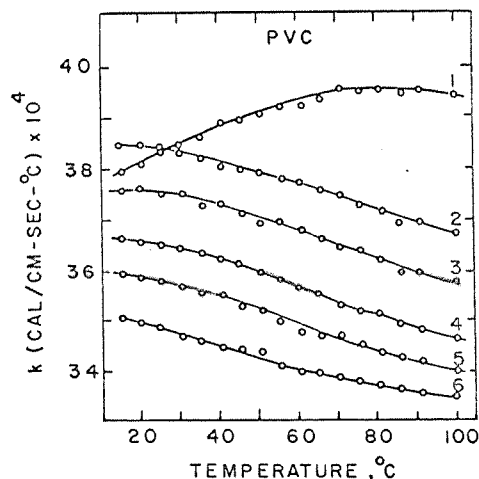


Figure 5-13. Thermal conductivity of polyvinyl chloride as a function of temperature [Sheldon and Lane (19)].

increasing plasticizer content. Hellwege, Knappe, and Semjonow (56) presented data for PVC (20, 40, and 60% plasticizer) from -150° to $+100^{\circ}\text{C}$. The sample with least plasticizer exhibited a slight broad peak (4.2×10^{-4} cal/cm-sec- $^{\circ}\text{K}$) near -65°C , while the sample containing 40% plasticizer exhibited a smaller peak (3.2×10^{-4} cal/cm-sec- $^{\circ}\text{K}$) at -40°C , and a sample containing 60% plasticizer exhibited no peak but merely decreased from 2.5×10^{-4} units at -130°C to 2.2×10^{-4} units at 100°C . Increased plasticizer decreased the conductivity at all temperatures.

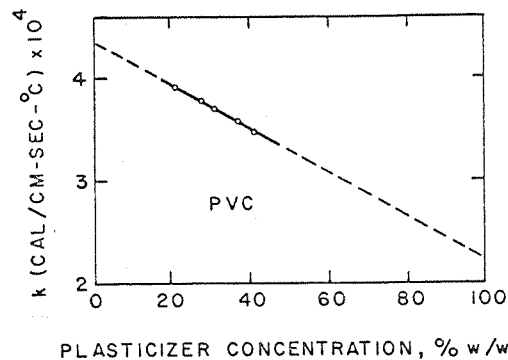


Figure 5-14. Thermal conductivity of polyvinyl chloride as a function of plasticizer concentration [Sheldon and Lane (19)].

Eiermann's(22) results for -190° to 90°C appear to differ from the above. With increasing plasticizer content (0, 10, 20, 40%) the conductivity peak shifts from the highest temperatures to -50°C . While increasing the percentage plasticizer causes a decrease in conductivity above the peak, it results in an increase in conductivity below the peak. This behavior is very similar to that observed by Sheldon and Lane(19). The reference of Eiermann and Hellwege(23) repeats these data. Steere(37) has also presented data for plasticized PVC.

Hellwege et al.(24) have measured the effects of stretching in the conductivity of PVC in directions parallel to and perpendicular to the stretch direction. (See also Fig. 5-8 of Section 5-3 for typical orientation results.) Diffusivity measurements of unplasticized PVC from 120° to 200°C can be found in Shoulberg's(10) work.

E. Polyethylene (PE)

Thermal conductivity behavior of polyethylene has been investigated extensively by Eiermann and co-workers(17,22,23,31,32,41,47,58,59) from -190° to about $+100^{\circ}\text{C}$ although an appreciable number of the publications apparently present repetitious data. Hattori(36,52,53,60) has reported k and α data for PE over the -60° to 120°C temperature range including studies of molecular weight. Cherkasova(54) reported results from 25° – 95°C ; Kirichenko et al.(46) reported results from 30° to 80°C ; Hansen and Ho(14) reported results for k , including the effect of molecular weight, for the temperature range 50° to 160°C ; Kline(55) reported results from 0° to $\sim 100^{\circ}\text{C}$; and Steere(62) has reported results from -50° to $+30^{\circ}\text{C}$ for α , k , and c_p .

Data of Eiermann(32) are given in Fig. 5-15 illustrating the increase in conductivity with increasing density of PE. Sheldon and Lane(61) obtained similar results, which illustrate the effect of increased density resulting primarily from increased crystallinity, as did Hansen and Ho(14), Tomlinson, Kline, and Sauer(16), and others. By a calculation based on the Maxwell equation for conduction in mixtures, Eiermann(32) has resolved the conductivity of PE into contributions from the amorphous and crystalline regions. The amorphous conductivity (Fig. 5-16) rises from about 3×10^{-4} cgs units at -190°C to a maximum of about 4.3×10^{-4} cgs units at -25°C . This behavior is somewhat similar to the conductivity behavior of amorphous PMMA cited earlier and is very similar to the results obtained on atactic (amorphous) polypropylene, as shown in Fig. 5-16. The conductivity of the crystalline regions (Fig. 5-17) follows approximately the T^{-1} behavior typical of molecular crystals.

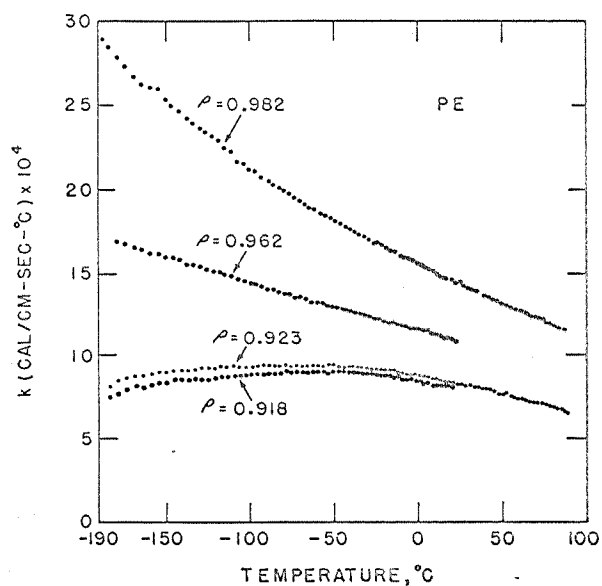


Figure 5-15. Thermal conductivity of polyethylenes ($\rho = 0.982, 0.962, 0.923, 0.918$) as a function of temperature [Eiermann(32)].

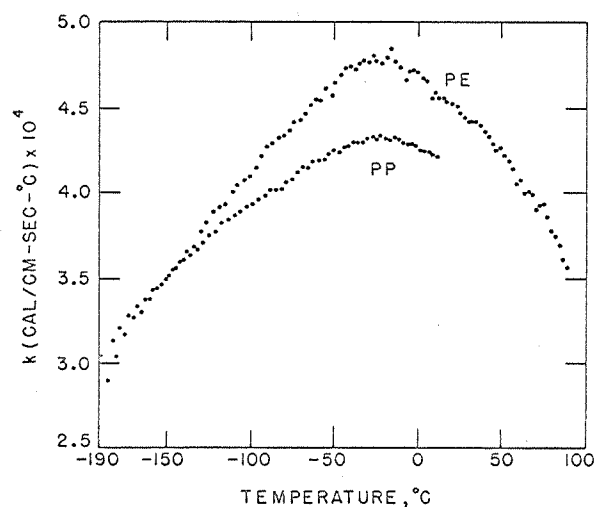


Figure 5-16. Thermal conductivity of atactic polypropylene and calculated thermal conductivity of amorphous polyethylene [Eiermann(32)].

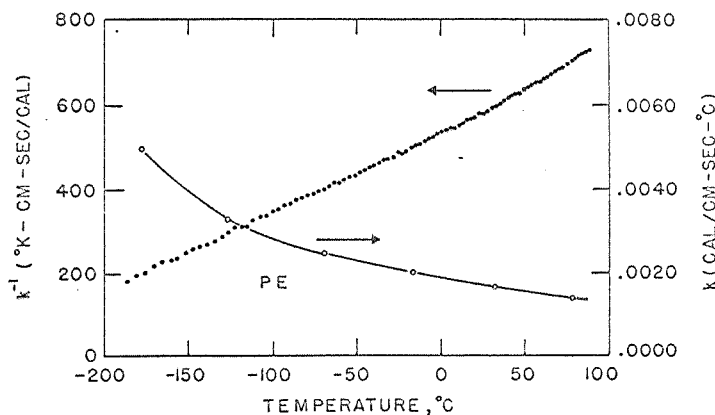


Figure 5-17. Calculated thermal conductivity and reciprocal conductivity of crystalline polyethylene [Eiermann(32)].

Reese and Tucker(51) have reported thermal conductivity data for PE below 5°K, showing that the conductivity tends towards zero with decreasing temperature. Shoulberg(10) has presented diffusivity data at high temperatures and in the melt. Hansen and Ho(14), Lohe(20), and Tomlinson, Kline, and Sauer(16) have measured the conductivity of polyethylene in the melt. The latter group obtained results by inducing slight cross-linking between molecular chains using nuclear radiation. Results indicate that the conductivity rises slightly with temperature in the melt and that the conductivity is higher for linear PE as compared to branched PE. Effects of radiation on the conductivity of polyethylene are discussed elsewhere. (See also Fig. 5-18.)

F. Polypropylene (PP)

Figure 5-19 is a plot of Eiermann's(31) data for isotactic partially crystalline PP ($\rho = 0.911 \text{ gm/cm}^3$) and atactic amorphous PP. Tomlinson and Kline(35) have reported data for isotactic PP ($\rho = 0.907$) showing that the conductivity decreases rather rapidly with temperature, similar to PE at higher temperatures, and approaches the conductivity value of the melt near the crystalline melting temperature (see Fig. 5-28 later in this section). Data on PP have been reported in other articles by Eiermann(32,41), Knappe(47), and Steere(37). The latter gives values of α , and c_p , and the k data exhibit an increase from about $3.2 \times 10^{-4} \text{ cal/cm-sec-}^\circ\text{C}$ at -100°C to about $7 \times 10^{-4} \text{ cal/cm-sec-}^\circ\text{C}$ near $+100^\circ\text{C}$.

Polypropylene data generally parallel PE data in that values for the

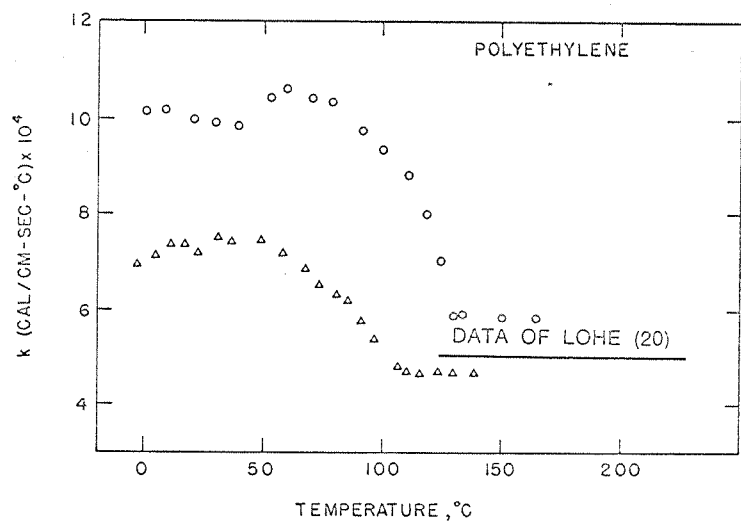


Figure 5-18. Thermal conductivity of polyethylenes at high temperatures [O, Δ , Tomlinson et al. (16); — Lohe (20)].

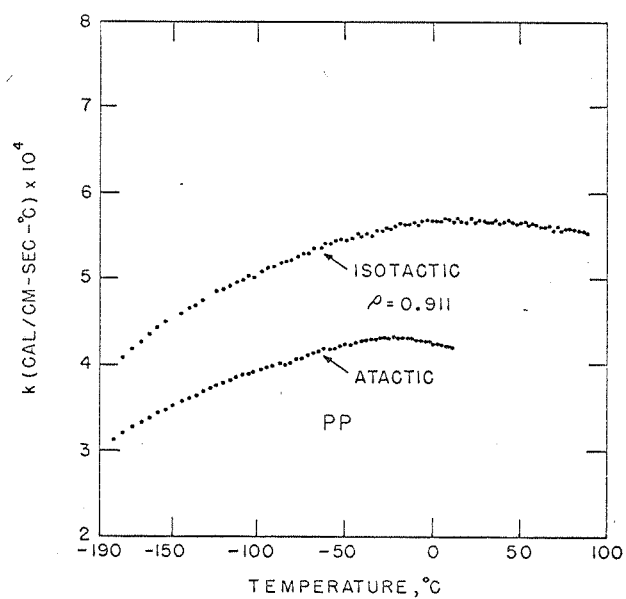


Figure 5-19. Thermal conductivity of polypropylene [Eiermann (31)].

amorphous material increase at increasing temperature to a maximum near the temperature of a glasslike relaxation (Fig. 5-16); the conductivity increases upon crystallization of the polymer; and at higher temperatures the conductivity decreases with increasing temperature as the crystallites melt, reaching the value of the molten polymer at the crystallite melting temperature.

Eiermann(31) has separated the conductivity of PP into amorphous and crystalline contributions by an analysis similar to that discussed for PE(32). The amorphous conductivity was similar to that for atactic PP; however, the conductivity was found to increase with increasing temperature contrary to that observed in PE.

G. Polyamides

Polyamides or nylons have been studied by a number of investigators including Hattori(63) (nylon 6, see Fig. 5-20); Kline(55) (nylon 66 from 0° to 100°C); Cherkasova(54) (nylon 68 from 25° to 95°C); Knappe(47) (nylon 6 and 610 from 20° to 100°C); and Holzmüller and Münx(45) (25° to 130°C). Reese and Tucker(51) obtained data on a nylon from 0.2° to 5°K, and Lohe(42) obtained data on nylon 6 in the melt from 210° to 240°C. In the melt the value was observed to be nearly temperature independent (5.2×10^{-4} cgs).

H. Polyoxymethylene

Data for polyoxymethylene have been reported by Eiermann(31) from -190° to +90°C and diffusivity data have been presented by Shoulberg(10) for Delrin in the melt. Eiermann's(31) results are shown in Fig. 5-21 for two materials ($\rho = 1.441$ gm/cm³ and $\rho = 1.432$ gm/cm³).

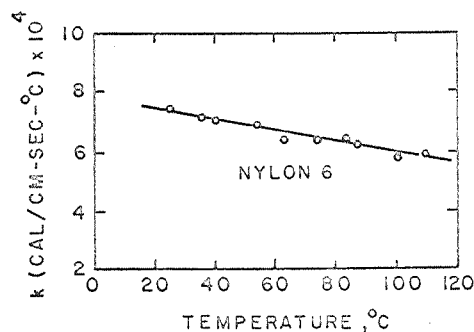


Figure 5-20. Thermal conductivity of nylon 6 as a function of temperature [Hattori (63)].

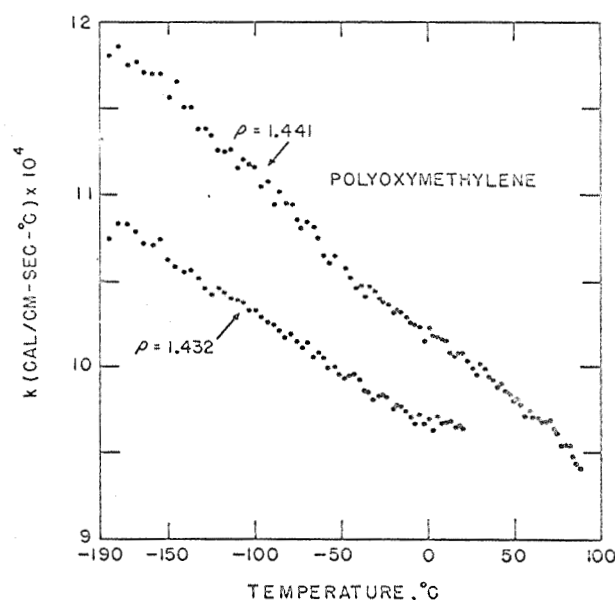


Figure 5-21. Thermal conductivity of polyoxymethylene as a function of temperature [Eiermann(31)].

The data show that the conductivity level is relatively high, that it decreases monotonically over the temperature range, and that it differs for materials of different density, the densities probably indicating different percentages of crystallinity.

I. Polyethylene Terephthalate (PETP)

PETP has been investigated by Eiermann and Hellwege(23) from -190° to $+80^{\circ}\text{C}$ and by Steere(37,62) from -150° to 120°C . Data of Eiermann and Hellwege(23), which are essentially repeated in references(22,31,41,58), are shown in Fig. 5-22 indicating that the thermal conductivity rises toward a maximum over the temperature range covered, and that the higher density material ($\rho = 1.409$) exhibits higher values of conductivity than the lower density material ($\rho = 1.337$). As in other partially crystalline polymers, this is probably a reflection of increased crystallinity.

Results of Steere(37,62) also show an increase in conductivity with increasing temperatures. Data for higher temperatures and for PETP in the melt are not reported.

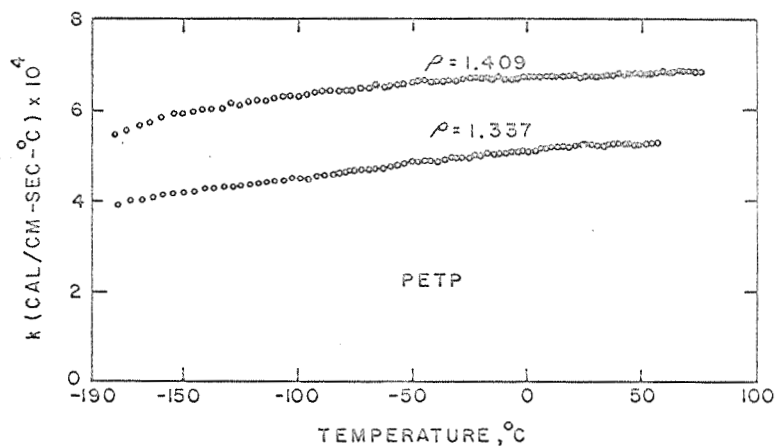


Figure 5-22. Thermal conductivity of polyethylene terephthalate [Eiermann and Hellwege(23)].

J. Polytetrafluoroethylene (PTFE)

The thermal conductivity behavior of PTFE has been studied by a number of investigators. It is considered to be especially interesting because, in addition to other known relaxations, it undergoes crystal-crystal transitions near 19° and 30°C, respectively. Steere's(37) conductivity data obtained by a dynamic technique (Fig. 5-23) show a

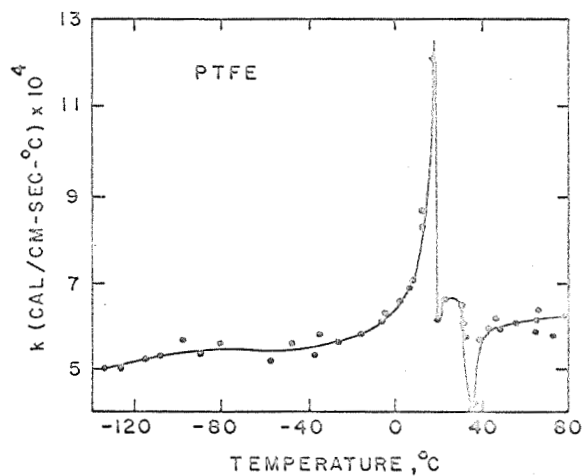


Figure 5-23. Thermal conductivity of polytetrafluoroethylene as a function of temperature [Steere(37)].

sharp rise above 0°C and an abrupt drop near 19°C. Following a slight recovery the data again show an abrupt drop near 30°C. Values(37) for α and C also exhibit dramatic changes with temperatures in the regions of the transition.

Eiermann and Hellwege(23) reported a drop in conductivity near 19°C. This work by Eiermann and associates can also be found in references(22,31,41,47,58). Hsu, Kline, and Tomlinson(34) also found changes occurring in the conductivity values in this temperature region. Results generally suggest that the conductivity tends to rise with increasing temperature below room temperature and that it is rather temperature independent from RT to about 120°C. At higher temperatures, it then decreases with temperature. Reese and Tucker(51) have reported a reasonably sharp increase in conductivity with temperature below 5°K, much as in other polymers. Powell et al.(64) have presented data for an investigation of PTFE from 5° to 90°C. Hattori(65) reported data for the 20°–100°C temperature region. Kirichenko et al.(46) reported data for the 30°–160°K range and Vasilev and Surkov(79) have presented c_p , k , and α data.

Conductivity studies of Hsu, Kline, and Tomlinson(34) suggest that relaxations present in PTFE may also affect the conductivity. Their data further indicate that, although quenching and annealing procedures changed the thermal conductivity, the conductivity level of both the quenched and annealed material was less than that of the as-received material. Furthermore, although the per cent crystallinity increased after a slight nuclear radiation dose, the conductivity decreased. Radiation effects data are discussed in another part of this section.

K. Polychlorotrifluoroethylene (PCTFE)

Reese and Tucker(51) investigated the thermal conductivity of PCTFE from $\sim 0.2^\circ$ to 5°K; Hattori(65) has reported data from 20° to 110°C for specimens of different percentages of crystallinity and has plotted conductivity vs. crystallinity for some percentages. Data of Eiermann(31) given in Fig. 5-24 show an increase in thermal conductivity from rather a low value of $\sim 2.4 \times 10^{-4}$ cal/cm-sec-°C at -190°C to a maximum of about 3.5×10^{-4} cal/cm-sec-°C near 75°C. Differences between the results for the two materials of different densities ($\rho = 2.097$ and $\rho = 2.112$ gm/cm³) are slight; but, above about -50°C , the conductivity of the denser material appears to be less than that of the less dense material. This is in contrast to Hattori's(65) results and results for many polymers which exhibit higher conductivity as the density increases.

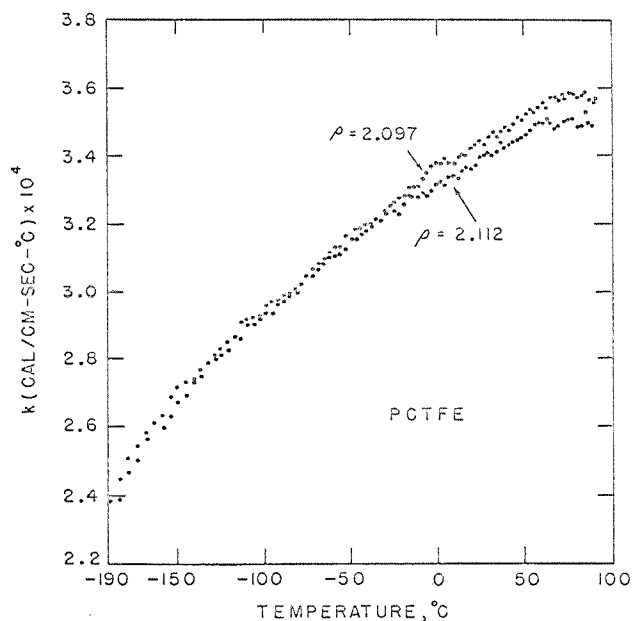


Figure 5-24. Thermal conductivity of polychlorotrifluoroethylene as a function of temperature [Eiermann(31)].

L. Thermosetting Polymers; Epoxies

Data on the thermal conductivity of epoxy systems and other thermosetting polymers have been reported by Cherkasova(54) for RT to $\sim 95^\circ\text{C}$, by Frielingsdorf(66), by Hertz and Haskins(67), by Eiermann and Knappe(68) as a function of filler; by Knappe(47) from 0° to 100°C , by Tsetlin, Yanova, Sibirskaya, and Rebinder(69) (bakelite and graphite system) as a function of filler concentration; and by Kline(55) for aluminum-filled epoxy systems from 0° to near 100°C . Data of Kline(55) are given in Fig. 5-25.

For the unfilled epoxy, diglycidyl ether of bisphenol A hardened with *m*-phenylene diamine(55), the conductivity rises slightly with temperature over the range studied. This is much as expected for an amorphous crosslinked polymer and is similar in character to results of Cherkasova in Fig. 5-12 (material specifications are not given) and not too different from the results of Knappe(47) which indicated a relatively constant conductivity of 4.8×10^{-4} cal/cm-sec- $^\circ\text{C}$ over the 0° – 100°C temperature range.

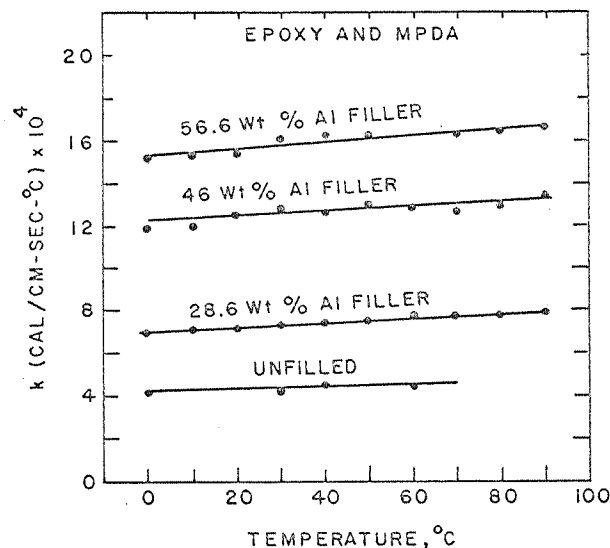


Figure 5-25. Thermal conductivity of aluminum-filled epoxy systems as a function of temperature [Kline(55)].

Addition of aluminum powder filler increased the conductivity but, as expected, the increase was not a simple arithmetic average of the conductivities of the aluminum and epoxy separately. The conductivity increased with filler content more rapidly than predicted by the Rayleigh-Maxwell equation for a dilute dispersion of spherical particles in a continuous medium. At all concentrations the epoxy apparently isolated the aluminum particles and maintained appreciable thermal resistance. From Fig. 5-25 it is noted that the conductivities of the filled systems increased slightly with temperature and there was some evidence that the data did not lie on straight lines but that there was some finer detail imposed on the over-all behavior.

M. Rubbers

Rubbers mentioned herein include both natural and synthetic forms although not nearly all the forms will be discussed. Carwile and Hoge (70) have studied conductivity data of the available literature to arrive at selected values for natural rubber. Their work provides an excellent source of references on the subject including the graphing of much of the data. Also, Anderson (71) has included rubber and cellular materials in a recent review discussing thermal conductivity in polymers.

Schallamach(72) has presented rubber data over the temperature range 100°–300°K while Eiermann and co-workers(22,23,29,40,41,56) have reported data from –190° to +90°C. Data of Eiermann and Hellwege(23) are given in Fig. 5-26, and it should be noted that some of the other references are only repeat data. Cherkasova(54) reported results for 25°–95°C, and Shoulberg(10) reported diffusivity data up to ~300°C.

Eiermann and Hellwege's(23) results indicate that data for natural rubber, crosslinked polyester-urethane, polyisobutylene, and silicone

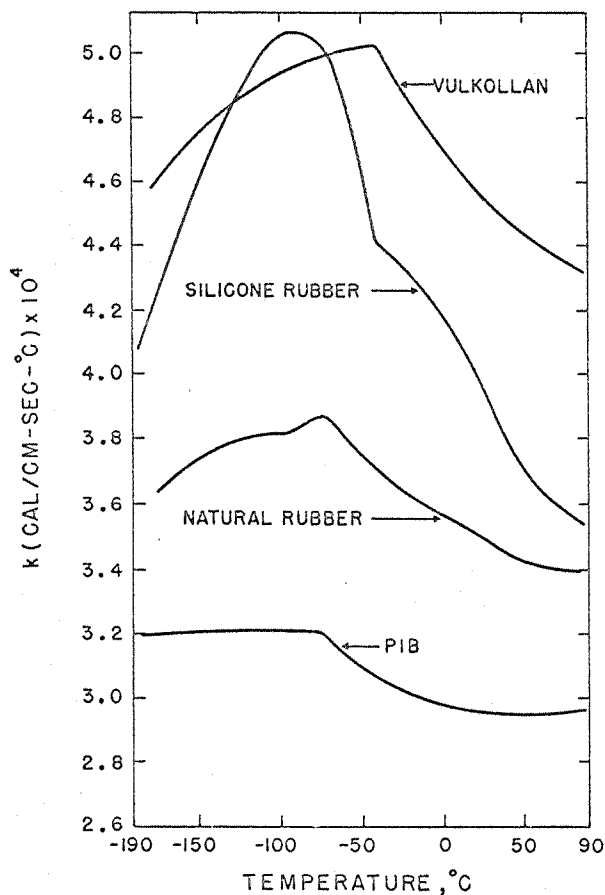


Figure 5-26. Thermal conductivity of natural rubber, polyisobutylene, silicone rubber, and Vulkollan (crosslinked polyester-urethane) as a function of temperature [Eiermann and Hellwege(23)].

rubber have a similar character in that for the most part the conductivity rises with increasing temperature up to the glass-rubber transition, then the values decrease with temperature, somewhat as in the case of the glass-liquid transition (PMMA). Actual conductivity levels depend upon the particular molecular structure. At higher temperatures it seems probable that the conductivity again rises with temperature. One would expect the results to be generally similar in some respects to those for polymer melts and epoxy systems at higher temperatures. Filled rubber systems have been studied, and data on some of these can be found in references(70,71).

N. Other Polymers

Some other polymers which have been studied but will not be treated separately include a polyester studied by Hattori(36,39); cellulose acetate and cellulose acetate butyrate studied by Knappe(47) from RT to 100°C; chlorosulfonated PE reported by Hennig and Knappe(29); vinyl chloride acetate copolymer reported by Hattori(52,74); and polybutene studied by Boggs and Sibbitt(75). Cherkasova(54) also reported data (25°–95°C) on miscellaneous other materials not heretofore discussed, including paraffin (see Fig. 5-12). Knappe(47) gave conductivity data for polyvinyl carbazol and polycarbonate (~20° to 100°C). Polycarbonate data are also presented by Hellwege, Hennig, and Knappe(24) and Steere(37), and diffusivity data are reported for polycarbonate in the melt by Shoulberg(10). Penton data are reported by Lohe(42) at temperatures into the melting region.

O. Irradiated Polymers

Changes in thermal conductivity resulting from nuclear radiation have been studied by Tomlinson et al.(16) for PE, Hsu, Kline, and Tomlinson(34) for PTFE, and Tomlinson and Kline(35) for PP. Hattori(36) has reported diffusivity results for γ -irradiated PE. Results(16) indicate that reactor radiation tends to break up the crystallites in PE, leading to decreased conductivity at lower temperatures, as can be observed in Fig. 5-27. Crosslinking occurs as a result of the irradiation but at lower temperatures this does not appear to compensate for the loss in crystallinity even though the crosslinking/scission ratio is relatively high. At higher temperatures, for instance above 100°C (see Fig. 5-27), higher doses result in an increase in conductivity level, probably resulting primarily from radiation-induced crosslinking.

Isotactic polypropylene is rather similar to PE in structure and typically has a relatively large percentage crystallinity. The crosslinking

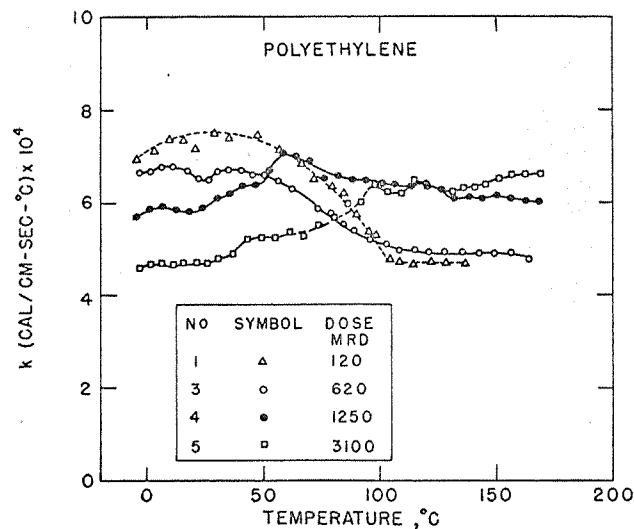


Figure 5-27. Effect of reactor radiation on the thermal conductivity of polyethylene [Tomlinson *et al.*(16)].

to scission ratio is much lower than in the case of PE. Upon γ -irradiation(35) the over-all conductivity level (0°–160°C) decreases, probably primarily as a result of disordering of crystallites. Results are given in Fig. 5-28. Differential scanning calorimeter data indicate that as the crystallites are increasingly disordered the temperature range of melting process broadens. The melting temperature shifts to lower temperatures with increasing radiation dose. It is interesting to note that, although radiation-induced crosslinking occurs in PP, the conductivity did not increase with dose, presumably largely because of the relatively small crosslinking/scission ratio.

Data for PTFE(34) showed that the thermal conductivity behavior following gamma irradiation differed substantially from both PE and PP (see Fig. 5-29). PTFE is relatively sensitive to radiation and the percentage crystallinity, as indicated by infrared measurements, increased with dose. However, the conductivity level decreased with increasing radiation dose.

5-5 CONDUCTIVITY MEASUREMENTS

Thermal conductivity measurement techniques can be conveniently divided into steady-state methods, where the conductivity measurement parameters are not changing significantly with time, and into

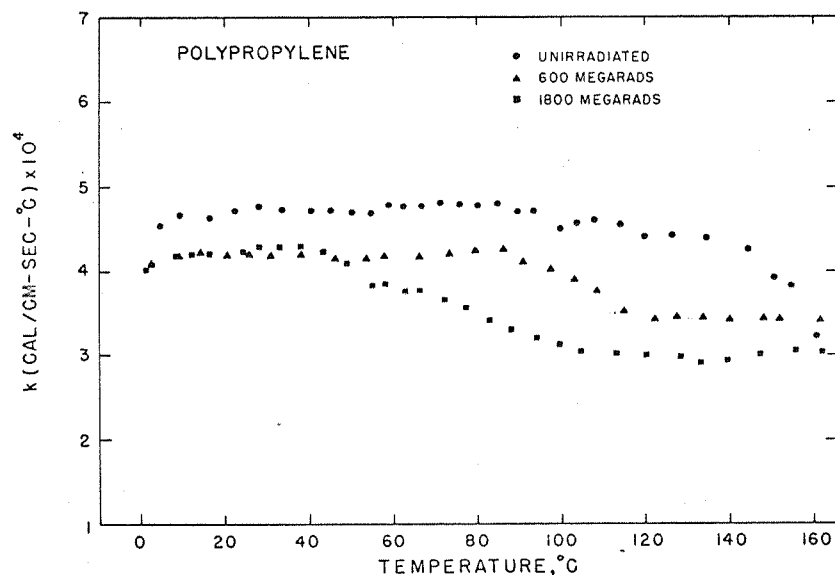


Figure 5-28. Thermal conductivity of γ -irradiated polypropylene as a function of temperature [Tomlinson and Kline(35)].

transient methods, where measurement parameters change rather rapidly with time. In the former it is customary to calculate the thermal conductivity of, say, a slab directly from an equation of the form

$$k = \frac{q \cdot d}{A \cdot \Delta T}$$

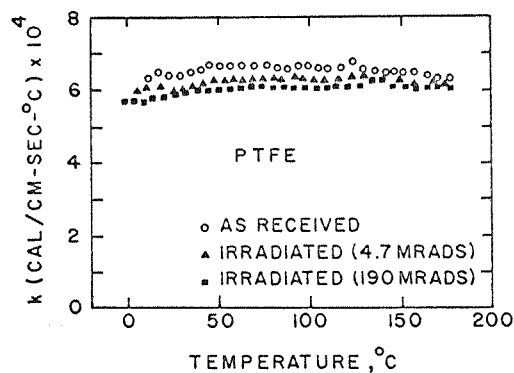


Figure 5-29. Thermal conductivity of γ -irradiated polytetrafluoroethylene as a function of temperature [Hsu *et al.*(34)].

where A is the area of the sample and d is the thickness. In the latter method the diffusivity α is usually the basic quantity calculated from the measurements because the thermal diffusivity is the property which determines time-dependent heat flow through the polymer material. Using the relation

$$k = \alpha \rho c_p$$

k is then deduced if α , ρ , and c_p are known. As will be pointed out in the following discussion, some types of apparatus have been designed to operate utilizing both techniques.

A. Steady-State Techniques

1. ASTM METHOD

Perhaps the best-known standard for measuring the thermal conductivity by steady-state techniques is that given by the American Society for Testing Materials(76). This method will be discussed first, then variations used by many research groups will be discussed along with some possible reasons for the variations employed.

Figure 5-30 is a diagram illustrating the basic features of the ASTM Designation C177-63 for the metal-surfaced hot plate. The heating section is composed of a round or square central heater A and similarly-shaped central surface plates B into which permanently installed thermocouples are set in grooves or just below the working surface. A guard section, composed of a guard heater C and guard surface plates D, surrounds the heating section and is isolated by a gap $\frac{1}{8}$ in. or less. The radial heat flow in the sample is minimized by adjusting the power inputs to heaters A and C such that the temperature differential between plates B and D is nearly zero. The detection system for this is required to be sufficiently sensitive to assure that the variation in conductivity due to gap temperature imbalance is restricted to less than 0.5%. Heat losses from the outer edges of the guard section and specimens are restricted by edge insulation or by governing the surrounding air temperature. Identical test specimens are placed between the central sections and the cooling units. Rigid and hard specimens are required to have parallel flat surfaces to within 0.003 in./ft, and all plates involved require similar flatness. Working surfaces of the heating unit and cooling plates are required to be smoothly finished and checked periodically for defects. Surfaces are to be treated to have a total emittance greater than 0.8 at all operating temperatures.

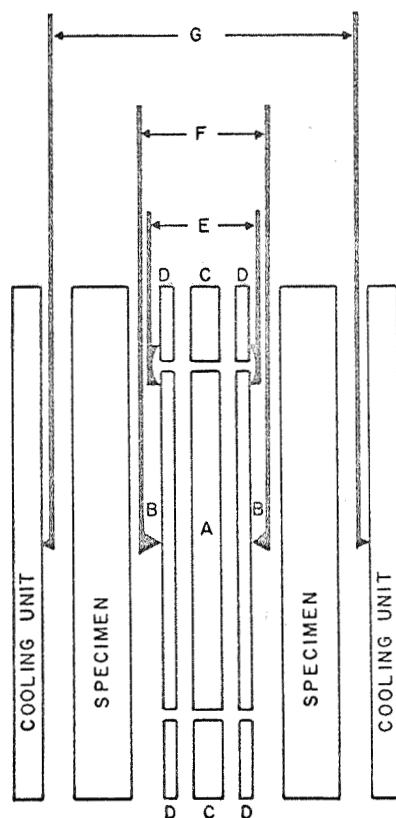


Figure 5-30. Schematic diagram for guarded hot plate cell: A, central heater; B, central surface plate; C, guard heater; D, guard surface plate; E, differential thermocouples; F, heating surface thermocouples; G, cooling unit surface thermocouples. [ASTM(76)].

A reproducible constant pressure is maintained between the plates and specimens to promote good thermal contact. The temperature differential between hot and cold plates is specified to be 10°F or more and, for good insulators, the minimum recommended gradient is 40°F/in. Fluctuations or changes in temperatures of the hot plate surfaces must not be more than 0.5% during a 1-hr test period. Temperatures of the cold plate surfaces are subject to the same limiting conditions.

Typical sample sizes can range from about 1-in. max. thickness with a central linear dimension of 4 in. and a 2-in. wide guard ring to a 4-in. max. thickness with a central linear dimension of 12 in. and a 6-in.-wide guard ring. The specification designates that, for practical purposes, the method is limited to specimens having thermal conductances of not more than 10 Btu/hr-ft²-°F and thickness conforming to the above. It would appear that the conductance limitation would very seldom affect most polymer systems.

ASTM Designation C177-63 described above provides for accurate repeatable thermal conductivity measurements for stable polymer systems. Woodside and Wilson(77) have reported on imbalance errors in the use of guarded hot plate measurements. If the conductivity is not changing with temperature or time and contact at the specimen surfaces is adequate, the measurements are absolute; however, the rather large specified temperature differential tends to average any rapid fluctuations of material conductivity with temperature, and the stringent conditions regarding the long-time steady-state conditions for measurement tend to obscure any conductivity changes occurring as a function of time. Using this method, heat losses are minimized and can be largely accounted for and measurements can be made over a rather wide temperature range (from near -100°F to values approaching 1300°F) according to the designation.

In studies of thermal conductivity which are primarily related to research, deviations from the ASTM method are often utilized for several reasons. New and/or special polymers and related materials are typically available only in relatively small quantities and multiple specimens may be required for experiments; thus the sample size must be small. Furthermore, measurements at extreme temperatures (for instance, below liquid nitrogen or liquid helium temperatures) may be of primary interest and small samples and small over-all dimensions tend to reduce some problems associated with measurements because losses are less and the entire system may be easily enclosed by a Dewar vessel or equivalent. In studies of variations of conductivity with a given parameter, such as with regard to temperature for instance, the temperature differential must be minimized if rather rapid changes are to be detected and analyzed. This too suggests that specimens should be rather thin. Since a very large number of experimental points are desired in most research, and specimens with varying histories and treatments are of interest, it is of the utmost importance to decrease the time per measurement to a point where the over-all time required for a given experiment is manageable and practicable. Thus very large times

required for equilibrium are sometimes reduced at the expense of accuracy in attaining absolute values.

2. TUBULAR GEOMETRY VARIATION

For thermal conductivity measurements of polymers above room temperature, a variation of the steady-state method reported by Kline (55) utilizes tubular samples formed from stock or molded to size. The volume of material per specimen is relatively small (~ 6 cc). Heat is supplied to a central copper rod by an imbedded heater and flows radially through the sample to an outside copper tube which is maintained at the desired temperature by a circulating coolant. Thermocouples in the inner and outer copper surfaces are used to measure the temperature drop across the specimen and the energy supplied to the heater is determined from voltage and current measurements.

3. PLATE METHOD FOR SMALL SPECIMENS

Eiermann and Knappe(68) and co-workers have described an apparatus in which a thin foil heater about $\frac{1}{100}$ mm is used as a resistance source to supply heat to dual samples which are about $80 \times 80 \times 3$ – 5 mm ($3.2 \times 3.2 \times 0.12$ – 0.20 in.). This sample size corresponds to ~ 19 cc minimum sample volume. For many polymers one can reach steady-state values to within 1% in 10 min when the power is turned on abruptly in the heater and the cold plates act as infinite heat sinks. Thus with proper controls one can obtain a reasonable number of data points per unit time in research studies. In the Eiermann and Knappe reference(68) metal blocks grip the heating foil at each end and supply electrical power evenly to the foil. Operation to satisfactory accuracy levels does not require the use of a guard ring.

Eiermann and Knappe(68) report results from -180° to $+50^\circ\text{C}$ which demonstrate the extreme importance of good thermal contact in obtaining reliable results, especially at lower temperatures. In another reference, Eiermann et al.(58) describe an apparatus in which the temperature rises slowly with time while thermal conductivity data are obtained. Heat input is measured by noting the rate of temperature rise of a copper disk whose mass and heat capacity are known.

Kreahling and Kline(78) have developed an apparatus similar to that of Eiermann and co-workers which utilizes samples which are typically 0.080 in. thick and 3 in. in diameter. However in this case heat is supplied by a foil which has a weaving conduction pattern etched into shape and requires only simple wire electrical connections. The temperature range is about -190° to $+100^\circ\text{C}$.

4. LOW TEMPERATURE METHODS

For thermal conductivity measurements of polymers in the general range of liquid helium temperatures and above, Berman(6) has described an apparatus which utilizes relatively small samples. Powell et al.(64) also have reported an apparatus and data for use at low temperatures. In this case a relatively long sample is used and a system of guard rings is utilized along the length of the specimen to reduce losses to acceptable values. Reese and Tucker(4,51) have presented data in the helium temperature range obtained with an apparatus which has features somewhat similar to those of the Berman(6) apparatus and the Reese and Tucker(51) apparatus. Thermal contact is made with a threaded copper plug screwed into the end of the sample.

Anderson(71) has recently presented a review article on the thermal conductivity of polymers along with some discussion of apparatus. A split-bar method which may be particularly convenient for measurements of conductivity in materials with relatively large k values is noted with other various methods which are useful in certain applications. The reader is referred to the Anderson(71) paper for further details.

B. Transient Techniques

A number of investigators have reported methods for obtaining thermal conductivity data of polymers by transient techniques. Vos(73) considered heat flow characteristics in cylindrical geometry for the determination of k . Jaeger(8) considered heat conduction in an infinite region bounded internally by a circular cylinder of a perfect conductor to propose techniques for determination of k and α . In Shoulberg's(10) work, diffusivity of polymer melts were obtained in experiments involving a constant rate of temperature rise of a metal block which enclosed the samples. Techniques are also noted in the review paper by Anderson(71) and others(54,56). Chung and Jackson(48) reported a rapid, versatile, simple and inexpensive technique for the determination of the diffusivity in cylindrical geometry. For use on such materials as PMMA and rocket propellents, cylindrical samples with length-to-diameter ratios greater than 8 closely approximated infinitely long samples for test purposes. From room temperature to below steam temperatures, temperature data as functions of time were taken following an abrupt change in ambient temperature of the specimen. From these data the diffusivity was calculated. Chung and Jackson(48) emphasized that heat exchange losses with the surroundings were rather unimportant in their method and that the technique was espec-

ially valuable for badly warped or distorted samples. At a later date Hattori(36) also reported the usefulness of a transient method involving cylindrical geometry in the determination of diffusivity in polymers.

Harmathy(43) has reported on transient methods for the determination of thermal properties of solids which offer the advantage of producing a very small thermal disturbance in the material during measurement. Using flat specimens, a hot or cold pulse is applied to the surface of the sample. [A similar radial heat flow method has been described by Vasilev and Surkov(79,80).] By measuring the temperature-time behavior of points elsewhere in the material, data can be obtained from which k and α can be calculated. Using these and the density, the specific heat can also be deduced. Harmathy's(43) work is a valuable reference for previous related work by others as well.

An important part of the basic Harmathy technique is the use of a very thin foil electrical resistance heater between two flat specimens. Also, the specimens can be composed of layers of film material. When the electrical power to the heater is abruptly turned on or turned off, the heat flux to the specimens responds almost immediately because the mass of the foil can be largely neglected. In two important papers by Steere(37,62) further refinements of the method are presented along with conductivity, diffusivity, and specific heat data for several polymers over the approximate temperature range of -180° to $+120^{\circ}\text{C}$. Steere(62) reported the use of 0.00025 in. constant heating foil in providing a constant heat flux, the reduction of measurement time from 400 sec to 4 sec, and the application of 0.005 edge welded copper-constantan foil thermocouples. With refinements typical sample dimensions of Steere's(62) work might be $3 \times 6 \times 0.4$ cm, a total sample volume of 14.4 cm^3 . The small sample volume is clearly an important advantage of his method.

ACKNOWLEDGMENTS

The authors are indebted to R. P. Krehling and B. D. Washo for assistance in surveying the literature.

Research on polymer thermal conductivity at The Pennsylvania State University and at Rensselaer Polytechnic Institute has been supported by the National Aeronautics and Space Administration.

SYMBOLS

C	heat capacity per unit volume, $\text{cal}/\text{cm}^3\text{-}^{\circ}\text{C}$
c_p	heat capacity, $\text{cal}/\text{gm-}^{\circ}\text{C}$
k	thermal conductivity, $\text{cal}/\text{cm-sec-}^{\circ}\text{C}$

q	heat flux, cal/cm ² -sec
T	temperature, °K or °C
t	time, sec
u	velocity of sound, cm/sec
v	specific volume
x, y, z	coordinate directions
x^*, y^*, z^*	principal axes directions
α	thermal diffusivity, cm ² /sec
β	linear thermal expansion coefficient
ρ	density, gm/cm ³
λ	phonon mean free path, cm
\parallel	subscript denoting direction parallel to stretching in an oriented polymer
\perp	subscript denoting direction perpendicular to stretching in an oriented polymer
0	as subscript denotes value for unoriented polymer
l	length, cm

REFERENCES

1. R. Berman, F. E. Simon, and R. L. Wilks, *Nature*, **168**, 277 (1951).
2. R. Peierls, *Ann. Physik*, **3**, 1055 (1929).
3. R. Berman, P. G. Klemens, F. E. Simon, and T. M. Fry, *Nature*, **166**, 864 (1950).
4. W. Reese, *J. Appl. Phys.*, **37**, 3227 (1966).
5. K. Eiermann, *Kunststoffe*, **51**, 512 (1961).
6. R. Berman, *Proc. Roy. Soc.*, **A208**, 90 (1951).
7. P. G. Klemens, *Proc. Roy. Soc.*, **A208**, 108 (1951).
8. J. C. Jaeger, *Australian J. Phys.*, **9-2**, 167 (1956).
9. H. L. Frisch and C. E. Rogers, *J. Polymer Sci.*, **C12**, 297 (1966).
10. R. H. Shoulberg, *J. Appl. Polymer Sci.*, **7**, 1597 (1963).
11. P. Lohe, *Kolloid Z. Z. Polymere*, **205**, 1 (1965).
12. A. C. Anderson, W. Reese, and J. C. Wheatley, *Rev. Sci. Instr.*, **34**, 1386 (1963).
13. K. Ueberreiter and E. Otto-Laupenmühlen, *Z. Naturforsch.*, **8a**, 664 (1953).
14. D. Hansen and C. C. Ho, *J. Polymer Sci.*, **A3**, 659 (1965).
15. D. Hansen, R. C. Kantayya, and C. C. Ho, *Polymer Eng. Sci.*, **6**, 260 (1966).
16. J. N. Tomlinson, D. E. Kline, and J. A. Sauer, *SPE Trans.*, **5**, 44 (1965).
17. A. Hennig, W. Knappe, and P. Lohe, *Kolloid Z. Z. Polymere*, **189**, 114 (1963).
18. K. Ueberreiter and S. Purucker, *Kolloid Z.*, **144**, 120 (1955).
19. R. P. Sheldon and K. Lane, *Polymer*, **6**, 77 (1965).
20. P. Lohe, *Kolloid Z. Z. Polymere*, **204**, 7 (1965).
21. H. Tautz, *Exper. Tech. Phys.*, **7**, 1 (1959).
22. K. Eiermann, *Kunststoffe*, **51**, 512 (1961).
23. K. Eiermann and K. H. Hellwege, *J. Polymer Sci.*, **57**, 99 (1962).
24. K. H. Hellwege, J. Hennig, and W. Knappe, *Kolloid Z. Z. Polymere*, **188**, 121 (1963).
25. K. Eiermann, *Kolloid Z. Z. Polymere*, **198**, 5 (1964).
26. K. Eiermann, *Kolloid Z. Z. Polymere*, **199**, 125 (1964).
27. J. Hennig, *Kolloid Z. Z. Polymere*, **196**, 136 (1964).
28. J. Hennig, *Kolloid Z. Z. Polymere*, **202**, 127 (1965).
29. J. Hennig and W. Knappe, *J. Polymer Sci.*, **C6**, 167 (1964).
30. B. D. Washo, Ph. D. Thesis, Rensselaer Polytechnic Institute, 1967.
31. K. Eiermann, *Kolloid Z. Z. Polymere*, **201**, 3 (1965).

32. K. Eiermann, *Kolloid Z. Z. Polymere*, **180**, 163 (1962).
33. R. P. Sheldon and K. Lane, *Polymer*, **6**, 205 (1965).
34. K. L. Hsu, D. E. Kline, and J. N. Tomlinson, *J. Appl. Polymer Sci.*, **9**, 3567 (1965).
35. J. N. Tomlinson and D. E. Kline, *J. Appl. Polymer Sci.*, **2**, 1931 (1967).
36. M. Hattori, *Kolloid Z. Z. Polymere*, **202**, 11 (1965).
37. R. C. Steere, *J. Appl. Polymer Sci.*, **10**, 1673 (1966).
38. W. Reese, *J. Appl. Phys.*, **37**, 864 (1966).
39. M. Hattori, *J. High Polymer Chem. (Japan)*, **19-201**, 32 (1962).
40. K. Eiermann, *Kolloid Z. Z. Polymere*, **198**, 5 (1964).
41. K. Eiermann, *J. Polymer Sci.*, **C6**, 157 (1964).
42. P. Lohse, *Kolloid Z. Z. Polymere*, **203**, 115 (1965).
43. T. Z. Harmathy, *J. Appl. Phys.*, **35**, 1190 (1964).
44. R. H. Shoulberg and J. A. Shetter, *J. Polymer Sci.*, **6-23**, 532 (1962).
45. W. Holzmüller and M. Münx, *Kolloid Z.*, **159**, 25 (1958).
46. Y. A. Kirichenko, B. M. Oleinik, and T. Z. Chadovich, *Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR*, **7** (5), 70 (1964).
47. W. Knappe, *Kunststoffe*, **51**, 707 (1961).
48. P. K. Chung and M. L. Jackson, *Ind. Eng. Chem.*, **46**, 2563 (1954).
49. K. Ueberreiter and S. Nens, *Kolloid Z.*, **123**, 92 (1951).
50. K. Ueberreiter and E. Otto-Laupenmühlen, *Kolloid Z.*, **133**, 26 (1953).
51. W. Reese and J. E. Tucker, *J. Chem. Phys.*, **43-1**, 105 (1965).
52. M. Hattori, *Bull. Univ. Osaka Prefecture*, **A9-1**, 51 (1960).
53. M. Hattori and O. Kamiike, *J. High Polymer Chem. (Japan)*, **15-157**, 285 (1958).
54. L. N. Cherkasova, *Zh. Fiz. Khim.*, **33**, 1929 (1959).
55. D. E. Kline, *J. Polymer Sci.*, **50**, 441 (1961).
56. K. H. Hellwege, W. Knappe, and V. Semjonow, *Z. Angew. Phys.*, **11-8**, 285 (1959).
57. L. C. K. Carwile and H. J. Hoge, *Tech. Rep. 66-27-PR*, U.S. Army Natick Laboratories, Natick, Mass., (April 1966).
58. K. Eiermann, K. H. Hellwege, and W. Knappe, *Kolloid Z.*, **174**, 134 (1961).
59. K. Eiermann, *Kolloid Z. Z. Polymere*, **198**, 96 (1964).
60. M. Hattori, *J. High Polymer Chem. (Japan)*, **17-183**, 432 (1960).
61. R. P. Sheldon and K. Lane, *Polymer*, **6**, 205 (1965).
62. R. C. Steere, *J. Appl. Phys.*, **37**, 3338 (1966).
63. M. Hattori, *J. High Polymer Chem. (Japan)*, **19-201**, 35 (1962).
64. R. L. Powell, W. M. Rogers, and D. O. Coffin, *J. Res. NBS*, **59**, 349 (1957).
65. M. Hattori, *Kolloid Z. Z. Polymere*, **185**, 27 (1962).
66. H. Frielingsdorf, *Chem. Ingr. Tech.*, **32**, 291 (1960).
67. J. Hertz and J. F. Haskins, *Adv. Cryogenic Eng.*, **10**, 163 (1965).
68. K. Eiermann and W. Knappe, *Z. Angew. Phys.*, **14**, 484 (1962).
69. B. L. Tsetlin, L. Yanova, G. K. Sibirskaya, and P. A. Rebinder, *Proc. Acad. Sci., USSR, Phys. Chem. Sect.*, **114**, 281 (1958).
70. L. C. K. Carwile and H. J. Hoge, *Tech. Rep. 66-49-PR*, U.S. Army Natick Laboratories, Natick, Mass., June 1966.
71. D. R. Anderson, *Chem. Rev.*, **66-6**, 677 (1966).
72. A. Schallamach, *Proc. Phys. Soc. (London)*, **53**, 214 (1941).
73. B. H. Vos, *Appl. Sci. Res.*, **A-5**, 425 (1955).
74. M. Hattori and O. Kamiike, *J. High Polymer Chem. (Japan)*, **15-156**, 215 (1957).
75. J. H. Boggs and W. L. Sibbitt, *Ind. Eng. Chem.*, **47**, 289 (1955).
76. American Society for Testing Materials, Designation C177-63.

77. W. Woodside and A. G. Wilson, *ASTM, STP*, 217, 32 (1957).
78. R. P. Krehling and D. E. Kline (Unpublished).
79. L. L. Vasilev and G. A. Surkov, *Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR*, 7 (6), 20 (1964).
80. L. L. Vasilev, *Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR*, 7 (5), 76 (1964).